Mercury capture from flue gas on regenerable sorbents

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Abstract

The aim of this work is to evaluate elemental Hg capture in presence of different compounds in flue gas by a honeycomb structured Au/C regenerable sorbent.

Results of mercury capture were obtained in a bench scale experimental installation working at high space velocities 25000 h^{-1} for sorbent, a retention temperature from 50ºC to 150ºC and a high inlet concentration of either 11 or 22 ppb. The influence of other species rather than mercury present in the simulated flue gas on the sorbent performance was tested, in particular the effect on both Hg oxidation in presence of gold and Au oxidation.

Introduction

Main Hg anthropogenic source is the fossil fuel combustion, mostly, coal [1]. Specific technologies for mercury capture are mainly based on the use of sorbents injected in the gaseous stream for Hg capture, and subsequently retained in the particulate matter control systems, rendering new toxic residues to be controlled. Activated carbon injection (ACI) technologies require a high C:Hg ratio to achieve the desired mercury removal level (> 90%), which results in a high portion cost for sorbent material. A major problem associated with ACI technology is that the commercial value of fly ash is sacrificed due to its mixing with contaminated activated carbon powder and the generation of high amount of toxic residue.

Carbon filter beds before stack present problems associated to the low affinity between non-treated carbons and elemental mercury as well as the pressure drop in the fixed bed. High efficiency sulphur doped carbons are used for Hg retention on fixed beds, but the problem of toxic wastes still remains.

Regenerable sorbents can accomplish high mercury retention as well as balance cost because of this regenerability. Elemental mercury amalgamated with gold. This amalgam is extremely stable at room temperature and decomposes at higher temperature leaving clean gold ready for further capture [2, 3]. In order to capture trace amounts of mercury it is necessary to have the gold in a form of large surface areas [4]. However, metal monolayer tends to aggregate into larger islands in micrometer sizes after repetitive Hg exposure and heating, which could lead to inefficient mercury capture [2, 4, 5]. The efficiency of the Au for the retention of mercury would be enhanced if nanometric particulate sizes of the metal could be achieved.

In this work Au/C sorbent was tested for mercury capture at different temperatures of operation in order to have a first approach to test to test different position in a coal power plant (ESP cold-side, after WFGD or before the stack). Moreover, the regenerability of the

novel sorbent was tested along several cycles of capture-regeneration. The influence of presence of other gases in the simulated flue gas on the performance of the Au/C sorbent was evaluated, both the influence on either Au chemical state or Hg oxidation.

Experimental

A commercial carbon monolith with honeycomb structure was used as support for gold deposition.

The method for gold deposition consists of the direct reduction of the gold salt by the own carbon material of the support. The salt used for gold deposition was $HAuCl_4 \cdot 3H_2O$. A solution of 40 mg/l of salt in ethanol/water (1:1 v/v) was forced to pass through the channels of the carbon monolith to try to achieve a homogeneous deposition of gold along the channels of the monolithic supports. The contact time of the dissolution passing through the channels of the monolith was 30 min. After gold deposition distilled water was pumped through the channels of the sorbents to remove the spare gold dissolution. Sorbents were vacuum dried at 30ºC for 30 min. Sorbents were finally undergone to a reducing thermal treatment (TTR) at 300ºC in a flow containing 4% H_2 during 1 h. Sorbent obtained was labelled as MC-Au-red.

Sorbent was characterized by different techniques. The bulk Au content of the sorbent was obtained by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The surface Au content was determined by Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX). The gold nanoparticle size distribution was obtained by image analysis (free software "Image J") of electron micrographs taken by Scanning Electron Microscopy with Field-Emission (FE-SEM) technique. The oxidation states of gold were analyzed by X-ray Photoelectron Spectroscopy (XPS).
After mercury retention, some sorbents were characterized by XPS, in order to detect possible changes in Au oxidation state and X-ray Diffraction (XRD) in order to test crystal modification of Au by Au-Hg alloy formation.

A bench scale installation (Figure 1) was used to determine the efficiency of the sorbents for mercury capture and the maximum retention capacity at different operation conditions. A permeation tube for mercury gives the desired Hg concentration. The mercury is analyzed on-line with an elemental mercury analyzer (VM3000). Moreover, the installation is provided with a tail-end train of flasks to allow the capture the mercury as well as its speciation (in the case of evidences of oxidation under the experimental conditions). The installation is built up with Teflon pipes and pieces (in the part of the installation where Hg is present) to prevent possible mercury attack to steel. More details of the experimental installation are given elsewhere [3].

For the study of the influence of temperature on Hg capture, breakthrough curves were obtained at space velocity $7x10^8$ h^{-1} (referred to the active phase), temperatures from 50ºC to 150ºC and Hg inlet concentration of 22 ppb in N_2. It was considered that saturation is reached at 95% saturation. Moreover, the amount of Hg retained at 20% and 80% of breakthrough was calculated from the integration of the breakthrough curve. The efficiency of Hg retention was calculated as the ratio between the amount of Hg retained by the sorbents at either 20% or 80% of saturation and the total amount of Hg fed into the reaction during this time. Some experiments were repeated to test reproducibility. Some of the exhausted sorbents after Hg capture were analyzed for Hg content in an automated mercury analyzer (AMA) from Leco, and the results were compared with those obtained by breakthrough curve integration.

The study of the influence of the presence of other gases in the simulated flue gas on the performance of the Au/C sorbent was evaluated at 120ºC temperature, 11 ppb Hg and space velocity $7x10^8$ h^{-1} (referred to the active phase).

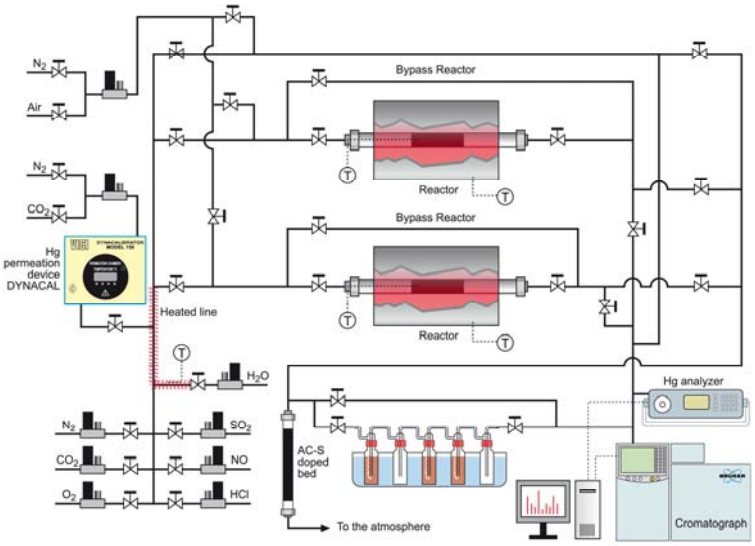

Figure 1. Experimental installation for Hg mercury tests.

Regeneration of exhausted sorbents was carried out at 220ºC during 1h. Details of regeneration process are given in [3]. After this period of time, the sorbent is cooled down to the desired temperature to be used in a new Hg capture test. Several cycles capture-regeneration were performed in order to test the efficiency for Hg capture along cycles.

Results and Discussion

The gold content in the bulk MC-Au-red sorbent was determined by ICP-OES and it was 0.11%. According to XPS studies, gold is mainly present as Au^0 after TTR at 300ºC.

The study of the distribution of gold along the monolith channels was carried out by SEM-EDX. Monoliths were longitudinal sectioned in order to determine the Au distribution along the channels. Seven measurement of gold content along each channel was carried out and an appropriate homogeneity of Au content was found. Moreover, different channels of a monolith and different monoliths were tested to obtain a representative value for Au surface content. The surface gold content from SEM-EDX for sorbent MC-Au-red was 3.96%.

In order to obtain the gold particle size distribution on the sorbents, several micrographs were taken by FE-SEM in backscattering mode. These micrographs were analyzed by image analysis using Image J free software. Average particle size (Feret's diameter) was 23 nm (diameter is 173 nm if smallest particles <10 nm are excluded because they just have a small contribution, 2%, to the area covered by individual particles).

Figure 2 shows breakthrough curves for MC-Au-red sorbent at different temperatures and initial Hg concentration in N_2 of 200 $\mu g/m^3$ as well as the amount of Hg captured (at 20 and 80% breakthrough).

At 20% breakthrough the Hg capture efficiencies are around 85% for all the temperatures studied. The highest temperature used for Hg retention gives low Hg retention capacity. This fact can be related with the low temperature needed to regenerate the sorbents, which was 220ºC [3]. Hg evolution started near 180ºC, which is close enough to the retention temperature of 150ºC.

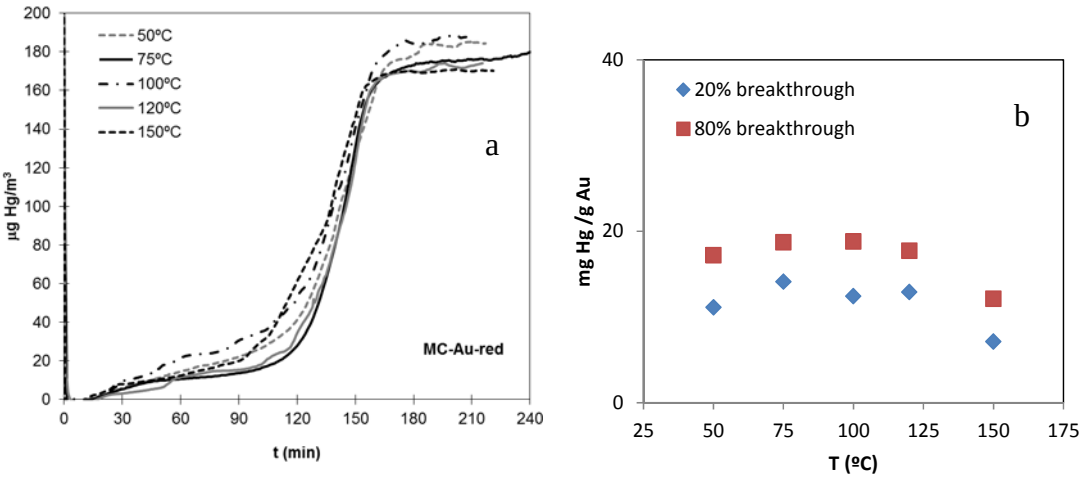

Figure 2. a) Hg breakthrough curves (initial Hg concentration 200 µg/m^3 in N_2); b) Amount of Hg captured at 20% and 80% breakthrough (initial Hg concentration 200 µg/m^3 in N_2).

Hg retention capacity was determined along several cycles of retention-regeneration at 75ºC initial Hg concentration in N_2 of 200 µg/m^3. Figure 3 shows the Hg retention capacity along several retention-regeneration cycles.

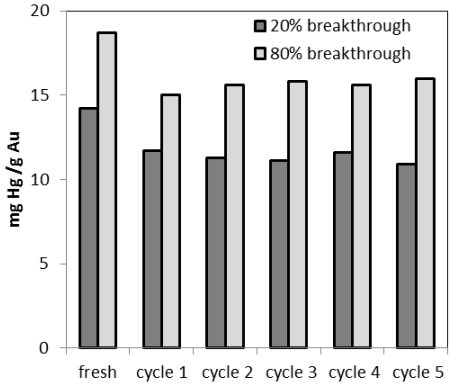

Figure 3. Amount of Hg captured along several capture-regeneration cycles by sorbent MC-Au-red.

The amount of Hg retained at 20% and 80% breakthrough decreases slightly after first regeneration and it is maintained along the cycles. This fact cannot be attributed to incomplete Hg evolution at 220ºC after 2h, that it was tested as complete. This fact can be explained in terms of some chemisorption on the support. This chemisorbed Hg remains on the sorbent after regeneration at 220ºC, meaning that no Hg will be retained by this mechanism after regeneration, because chemisorption sites are still occupied. This fact could explain the slight loss in Hg retention capacity after first regeneration. However, after first cycle the amount of Hg retained is similar to the amount retained in the rest of the cycles

tested, because the amalgamation capacity is maintained and the sites for chemisorption are yet occupied.
After Hg exposition, sorbent MC-Au-red was characterized in order to follow possible changes in gold. The exposition to mercury has not changed the XRD pattern of gold. As it was previously discussed [3] the mercury capture on the Au/C sorbent is based on the amalgam mechanism, so displacement of Au peaks was expected because of the formation of Au-Hg amalgam [6]. However, in present case the relation Hg/Au (=0.02) is low and this should be the reason of no new peaks appearing and no intensity of peaks decreasing. Assuming that the most probable Au-Hg amalgam formed is Au_3Hg (relation Hg/Au 0.33), the Au capacity for Hg of sorbent is not reached by far. This fact could confirm the need of lower Au particle size to take advantage of points of defects on Au crystal structure where Hg can be adsorbed.

Because of XRD is a bulk technique and it is difficult to follow changes when concentration of sample elements are low, the study of the surface of sample MC-Au-red before Hg exposition, after Hg exposition and after in-situ regeneration at 220ºC was carried out by XPS. Binding energy regimes containing the Au 4f and Hg 4f emission lines were obtained. The position of peak corresponding to Au 4f after Hg exposition is slightly shifted to higher binding energies. This shift has been reported by others [7] related with the amalgam formation. Hg content is at% 0.13 and Au content is at% 5.25, resulting in a Hg/Au ratio of 0.025, close to that obtained from breakthrough curves, as it has been reported above. Once the Hg and Au XPS spectra have been acquired, sample was heated up in situ at 220ºC during 2 h to remove Hg from sorbent. After cooling down to room temperature, a new XPS spectrum was obtained in order to follow possible changes on Au emission line. No displacement of Au 4f peak position from fresh sample is observed, indicating that Au/C sorbent is not altered by Hg capture-regeneration. These results agree with those obtained from breakthrough curves along Hg capture-regeneration cycles.

The influence of the presence of O_2 and SO_2 in the gas stream on Hg capture capacity of the sorbent MC-Au-red was studied separately. On one hand, Hg breakthrough curves were obtained in experiments carried out at 120ºC and initial Hg concentration in N_2 of 100 $\mu g/m^3$ with gas mixtures containing: Hg-5% O_2, Hg-2500 ppmv SO_2 and Hg-5%O_2-2500 ppmv SO_2 (rest inert gas). After experiments the oxidation state of Au as well as changes in the carbon support were followed by XPS. On the other hand, XPS in-situ studies were carried out in order to follow changes in Au 4f emission lines due to the treatment with different gases. Accordingly, a spectrum of MC-Au-red fresh sample was obtained. After that, the sample was moved to a catalytic chamber, where sample was treated with either 5% O_2 or 2000 ppm SO_2 or 2000 ppm SO_2+5% O_2 at two different temperatures 50º and 120ºC during 2 h. After the treatment, the sample was moved again to the analysis chamber and a new spectrum was obtained.

The in-situ treatment of sorbent in the XPS chamber shows that there are not changes on Au oxidation states regarding fresh sample. On the other hand, Au on sample after Hg experiments under same gas conditions does not undergo changes in the oxidation state of Au. This fact means that the sorbent is unaltered along experiments.

The possible oxidation of Hg^0 in presence of other gas components over Au, that can act as oxidation catalyst was studied by following Hg^{2+} specie. The presence of O_2 does not influence the Hg capture capacity of the sorbent and no Hg^{2+} is detected on the impingers train. With the presence of O_2 and SO_2 in the gas, the Hg capture capacity is reduced by 10%.

Because the sorbent is not altered by the composition of gas (as it is stated previously) that means that some part of Hg is oxidized to Hg^{2+} that is recovered in the KCl impingers. The amount of oxidized Hg was analysed in the AMA, and the value is near the loss of capture capacity by the sorbent.

Acknowledgements

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